Solid State Chemistry
CHEM-E4155 (5 cr)

Spring 2019

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Course outline

- **Teacher:** Antti Karttunen
- **Lectures**
  - 16 lectures (Mondays and Tuesdays, 12:15-14:00)
  - Each lecture includes a set of exercises (a MyCourses Quiz)
  - We start the exercises together during the lecture (deadline: Sunday 23:59)
- **Project work**
  - We create content in the Aalto Solid State Chemistry Wiki
  - Includes both independent and collaborative work (peer review)
  - Lots of content has been created in the Wiki during 2017-2018.
- **Grading**
  - Exercises 50%
  - Project work 50%
- **Workload (135 h)**
  - Lectures, combined with exercises 32 h
  - Home problem solving 48 h
  - Independent project work 55 h

Honor code for exercises

- The purpose of the exercises is to **support your learning**
- Most of the exercises are graded automatically
  - Some of the more demaning exercises I will grade manually
- It is perfectly OK to discuss the exercises with the other students
  - In fact, I encourage discussion during the exercise sessions
- It is **not OK** to take answers directly from the other students
  - This also means that is **not OK** to give answers directly to the other students
- The exercise answers and timestamps are being monitored

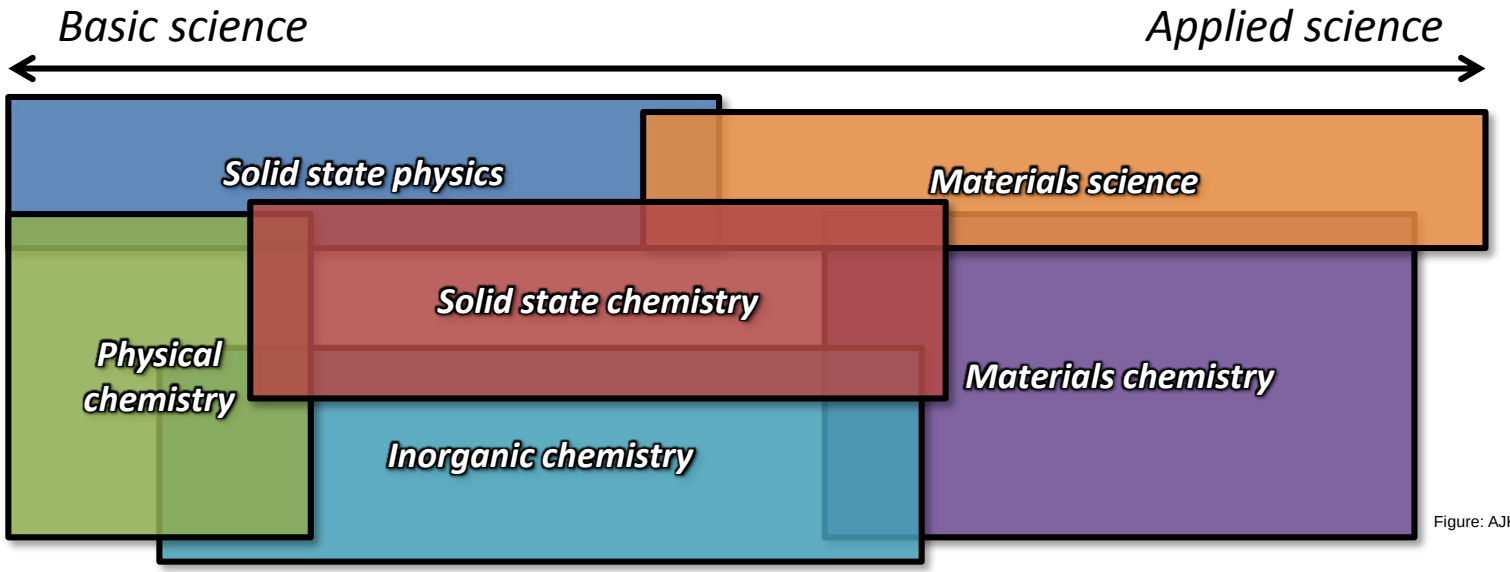
Course calendar

Mondays: 12.15 – 14.00
Tuesdays: 12.15 - 14.00

Week	Lect.	Date	Topic
1: Structure	1	25.2.	Structure of crystalline materials. X-ray diffraction. Symmetry.
	2	26.2.	Structural databases, visualization of crystal structures.
2: Bonding	3	4.3.	Bonding in solids. Description of crystal structures.
	4	5.3.	Band theory. Band structures.
3: Synthesis	5	11.3.	Solid state synthesis. Phase diagrams.
	6	12.3.	High-pressure synthesis, crystal growth, thin films.
4: Characterization	7	18.3.	XRD, Miller indices. Powder XRD databases. Microscopies
	8	19.3.	Spectroscopies and thermal analysis.
5: Main groups	9	25.3.	Abundance of elements, geochemistry, minerals.
	10	26.3.	Main group compounds, allotropes, Zintl phases.
6: *d*-block metals	11	1.4.	*d*-block metals, ligand field theory, magnetism.
	12	2.4.	*d*-block metal oxides and other compounds.
7: Specialized topics I	13	15.4.	Defects, non-stoichiometric oxides.
	14	16.4.	Semiconductors, doping, electrical properties.
8: Specialized topics II	15	23.4.	Tuesday. Layered compounds, intercalation chemistry, diffusion in solids.
	16	24.4.	Wednesday. Summary of all course topics. Project work checkpoint.

Solid state chemistry

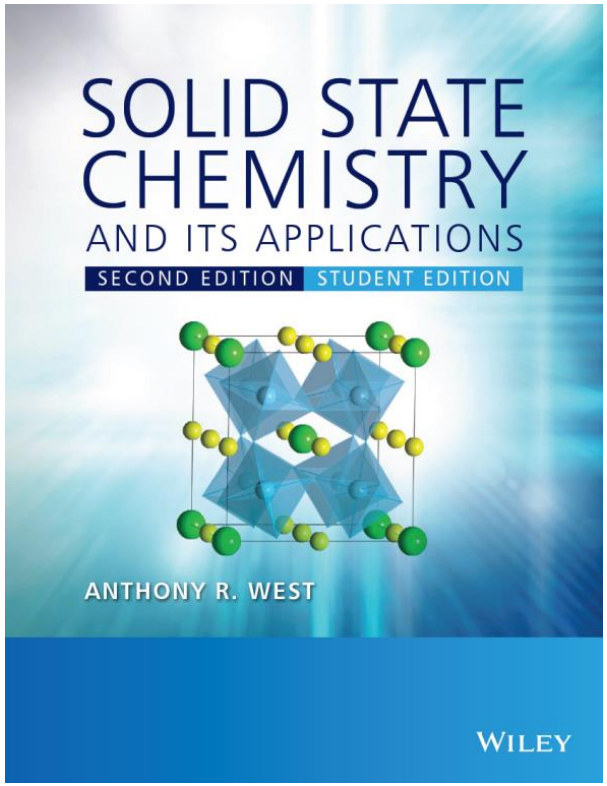
- Synthesis, structures, properties, and applications of crystalline inorganic materials

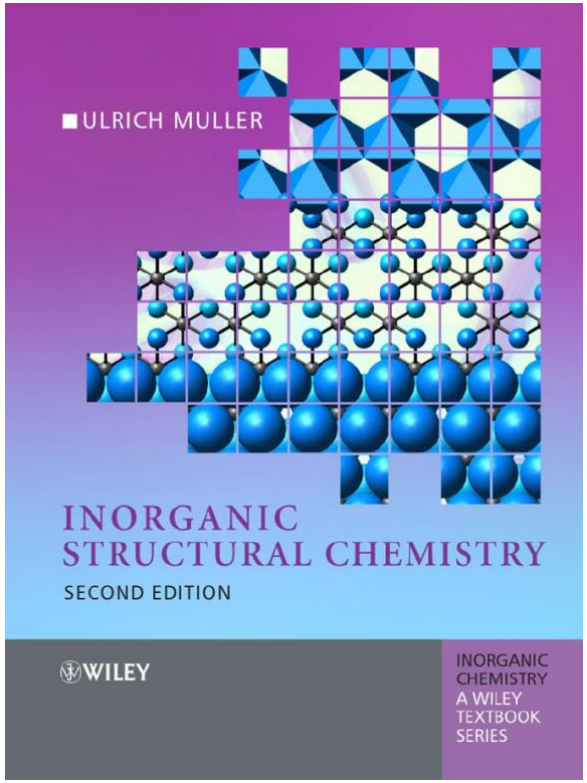


- ***Atomic-level structure*** of materials is at the very heart of solid state chemistry
- *"If you want to understand function, study structure"*
  - ***Francis Crick*** (1962 Nobel Prize in Physiology or Medicine – Structure of DNA)
- The above classification is a rather traditional one: new concepts such as ***metal-organic frameworks*** are bringing organic/organometallic chemistry into the picture
- What is ***your*** background? Chemistry, materials science, something else?

Literature

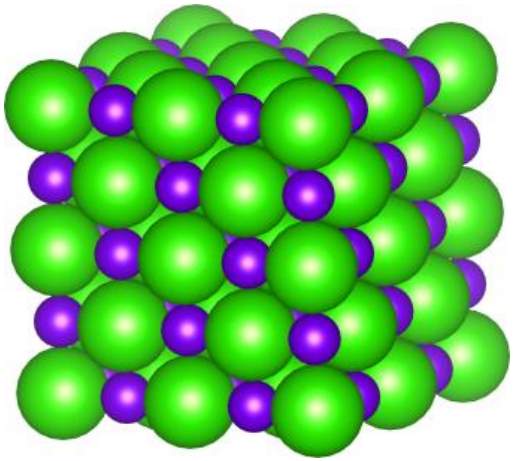
- *Solid State Chemistry and its Applications* – Student Edition (2nd ed.), Anthony R. West, **2013**, Wiley.
- *Inorganic Structural Chemistry* (2nd ed.), Ulrich Müller, **2006**, Wiley
  - (*Anorganische Strukturchemie* (fünfte Ed.), **2006**, Wiley)

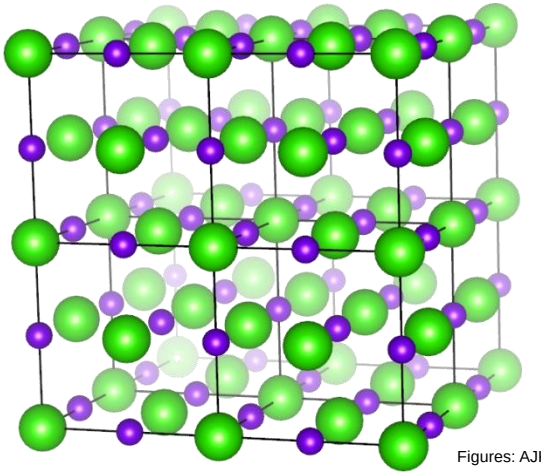




Lecture 1:
Structure of crystalline materials

- Basics of crystalline materials
  - Dimensionality of solids
  - Molecular vs. non-molecular solids
- X-ray diffraction
- Unit cell
- Crystal systems
- Symmetry
  - Point group symmetry and translational symmetry
  - Crystal classes
- Lattice
  - Lattice types and Bravais lattices
- Space groups

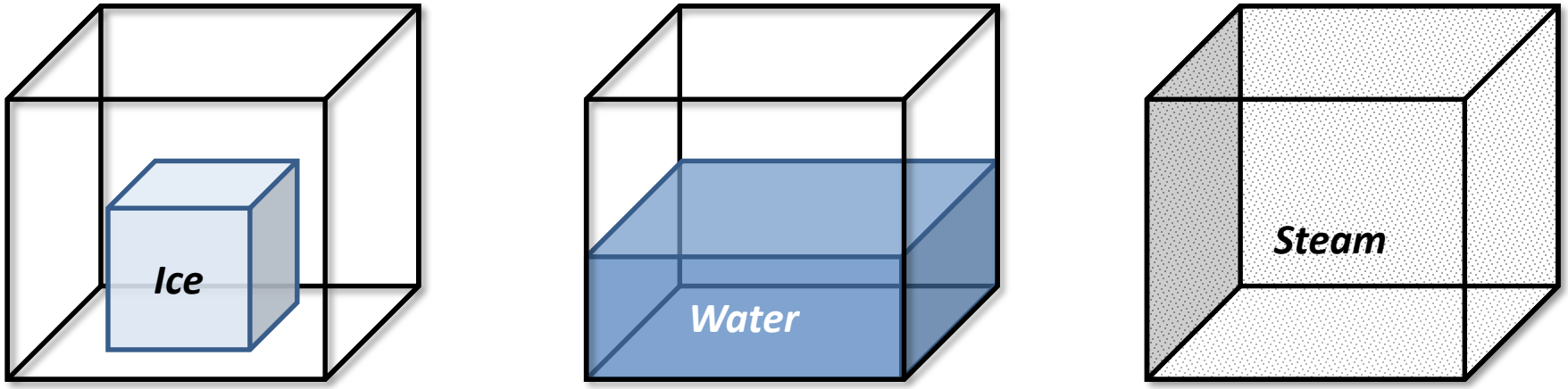




Figures: AJK

States of bulk matter

Temperature increases



Figures: AJK

Solid: Adopts and maintains a shape that is independent of the container it occupies.

Liquid: Adopts the shape of the part of the container it occupies and is separated from the unoccupied part of the container by a definite surface.

Gas: immediately fills any container it occupies

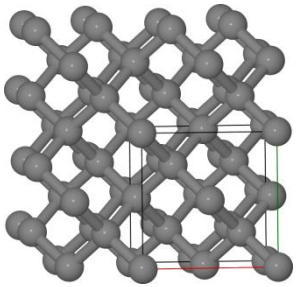
Condensed matter

Fluids (flow in response to forces such as gravity)

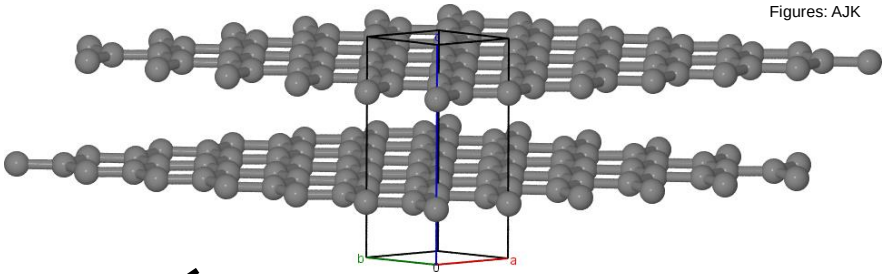
Molecular chemistry

Ref: Atkins' Physical Chemistry, 9th ed. p. 4

Dimensionality of solids



Two allotropes of carbon



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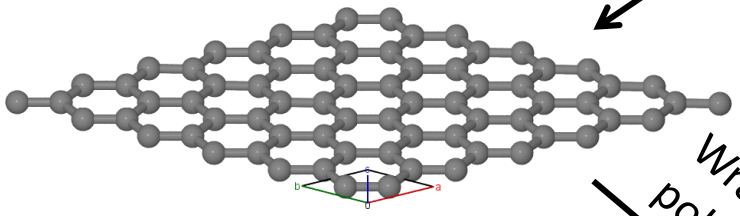
Diamond (3D)

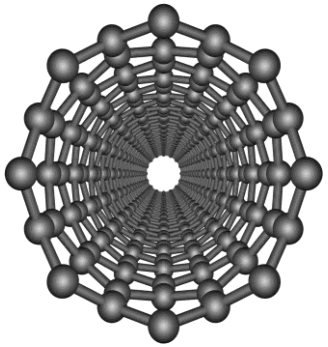
Graphite (3D)

Cut a slab



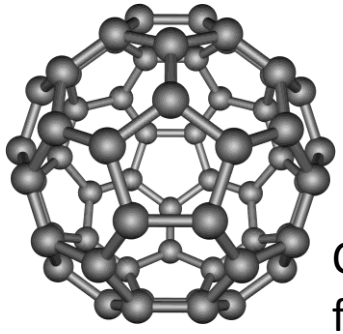
Graphene (2D)

Roll up to a tube



Carbon nanotube (1D)

Wrap up to a polyhedron



Carbon fullerene (0D)

Crystalline vs. amorphous

- Crystalline material
  - A material is a crystal if it has essentially a ***sharp diffraction pattern*** (IUCr definition)
- The definition includes
  - Periodic crystals
  - Aperiodic crystals
  - Quasicrystals
- ***Periodic*** crystal is a ***regular*** arrangement of atoms in three dimensions. These include
  a) Single crystals
  b) Polycrystals composed of many crystallites
- Amorphous materials
  - Non-crystalline
  - Lack long-range order
  - Not discussed on this course

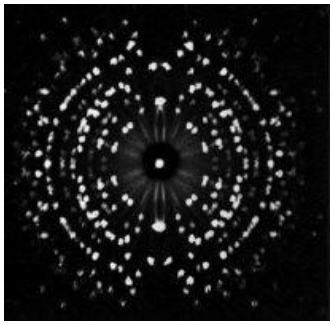


Figure: Susan Lehman / physics.wooster.edu

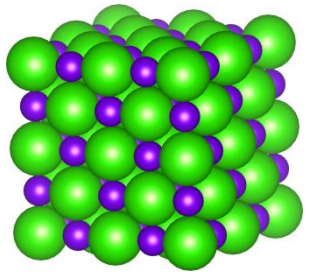
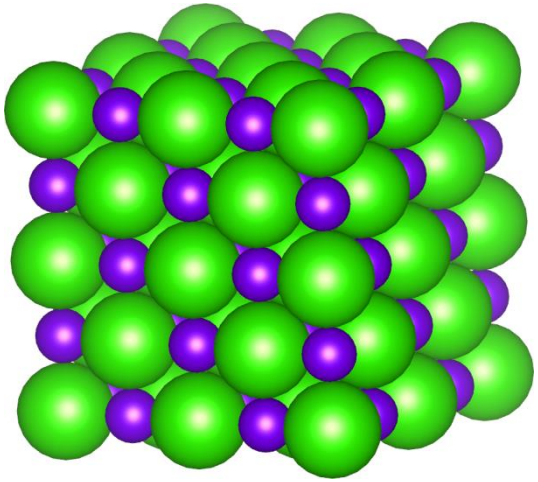


Figure: AJK

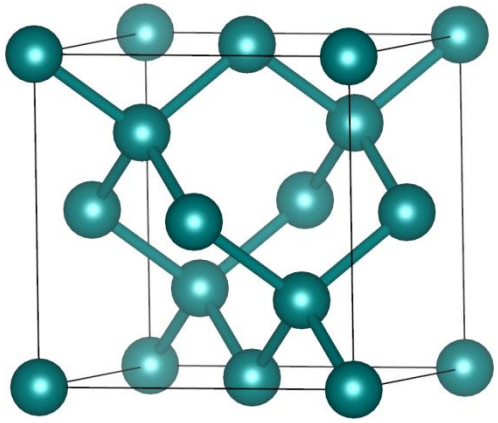
Photo: Virve Karttunen, 2009

Silicon single crystal grown by ***Czochralski process*** (*Deutsches Museum, München*)

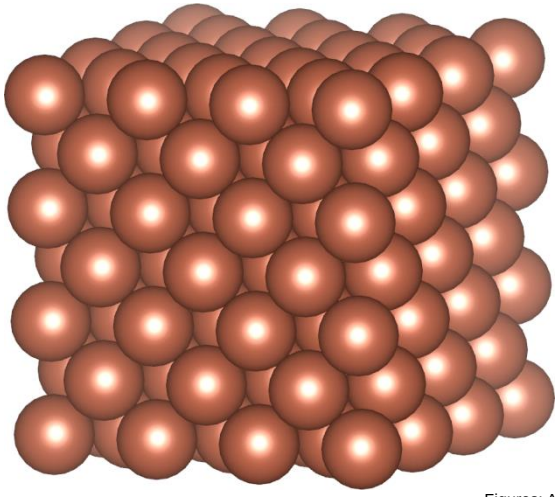
Non-molecular crystalline solids



Ionic bonding
(*e.g.* NaCl)



Covalent bonding
(*e.g.* silicon)



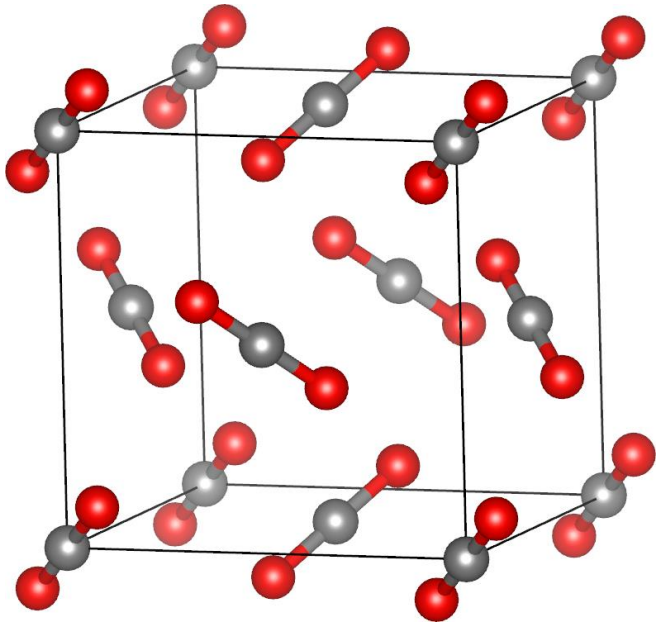
Figures: AJK

Metallic bonding
(*e.g.* copper)

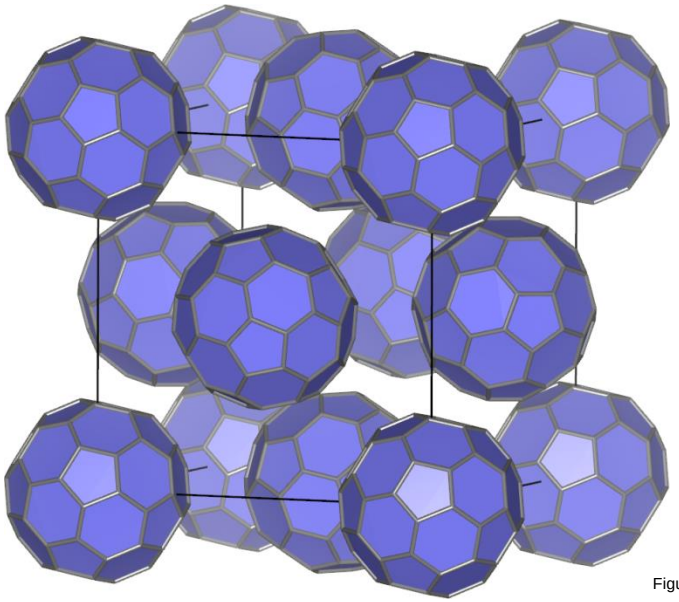
- Coordination polymers such as ***metal-organic frameworks*** show covalent bonding of metal atoms and organic molecules
- They are challenging the traditional classifications of solid state structures (see *e.g.* review of H. Furukawa *et al.*, *Science* **2013**, *341*, 1230444).

Molecular crystalline solids

- Composed of molecules that are held together by (weak) van der Waals forces
- Discussed only little here, but can be interesting for intercalation chemistry
- Much more relevant for small-molecule chemistry
- ***Crystal engineering*** using *e.g.* ***hydrogen*** and ***halogen*** bonding is making the boundary between molecular and non-molecular solids less clear!



Solid CO_2 (space group *Pa*-3, #205)
Acta Cryst. B **1980**, *36*, 2750.



Figures: AJK

Solid C_{60} (space group *Pa*-3, #205)
Nature **1991**, *353*, 147.

Structure of non-molecular crystalline solids

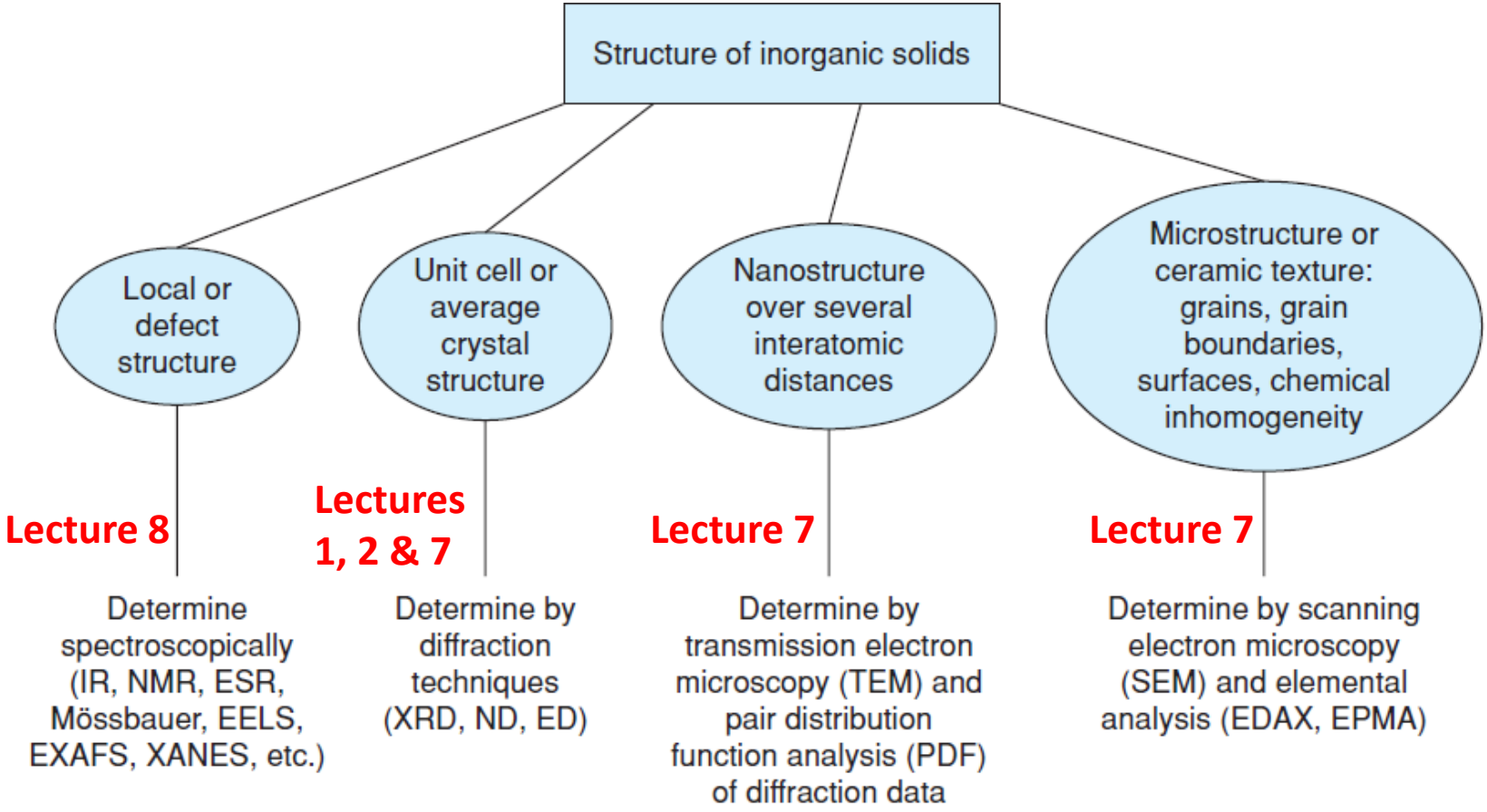


Figure 5.1 ***Structural features of inorganic solids across the length scales and some of the techniques used to study them.***

Ref: West p. 230

X-ray diffraction (1)

- X-rays are electromagnetic radiation of wavelength ~1 Å (10^{-10} m)
  - Matches the scale of atomic-level structure!

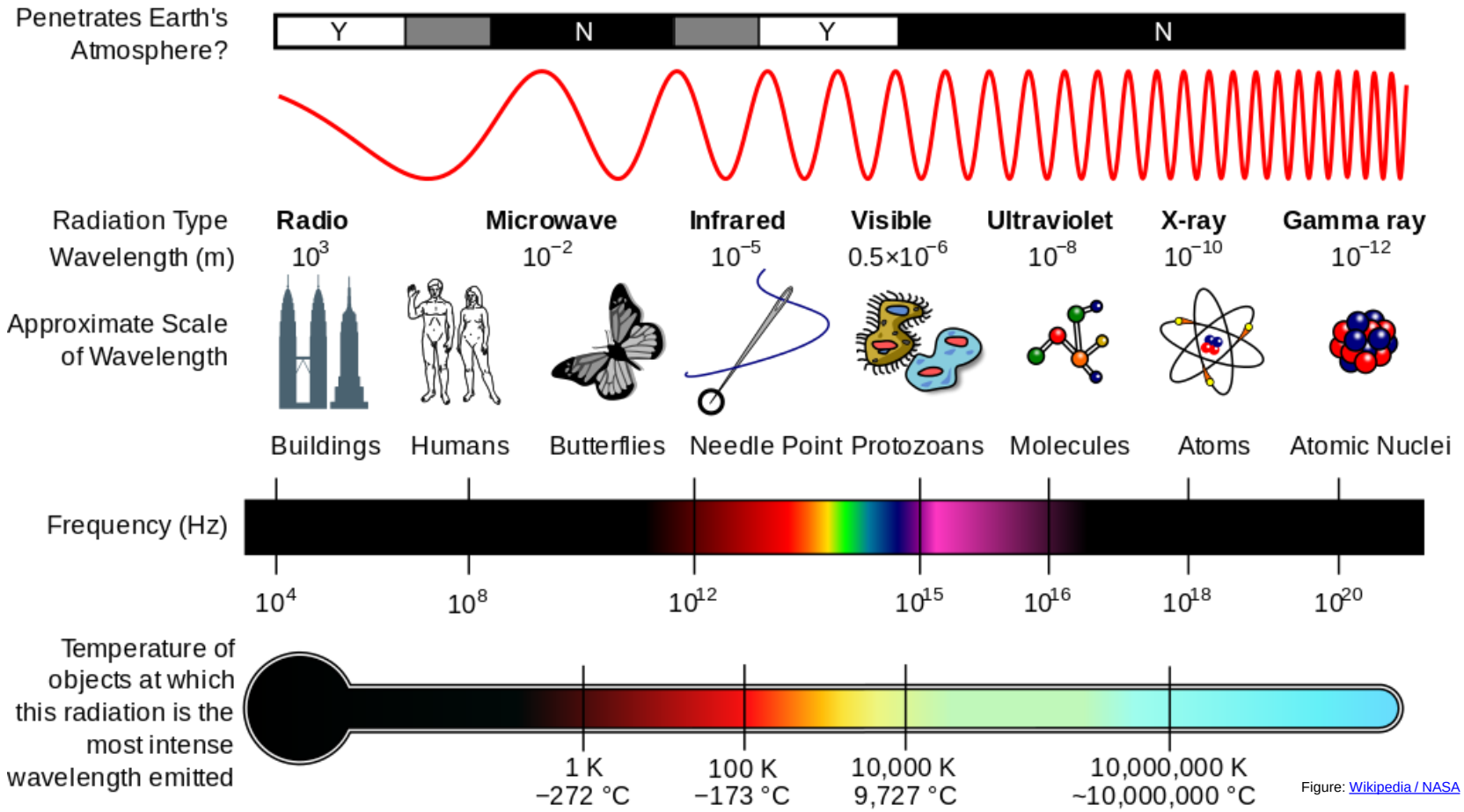


Figure: Wikipedia / NASA

X-ray diffraction (2)

- X-rays are produced when high-energy charged particles, *e.g.* electrons accelerated through a voltage of 30 000 V, collide with matter
- For X-ray diffraction experiments, we use *monochromatic* X-rays

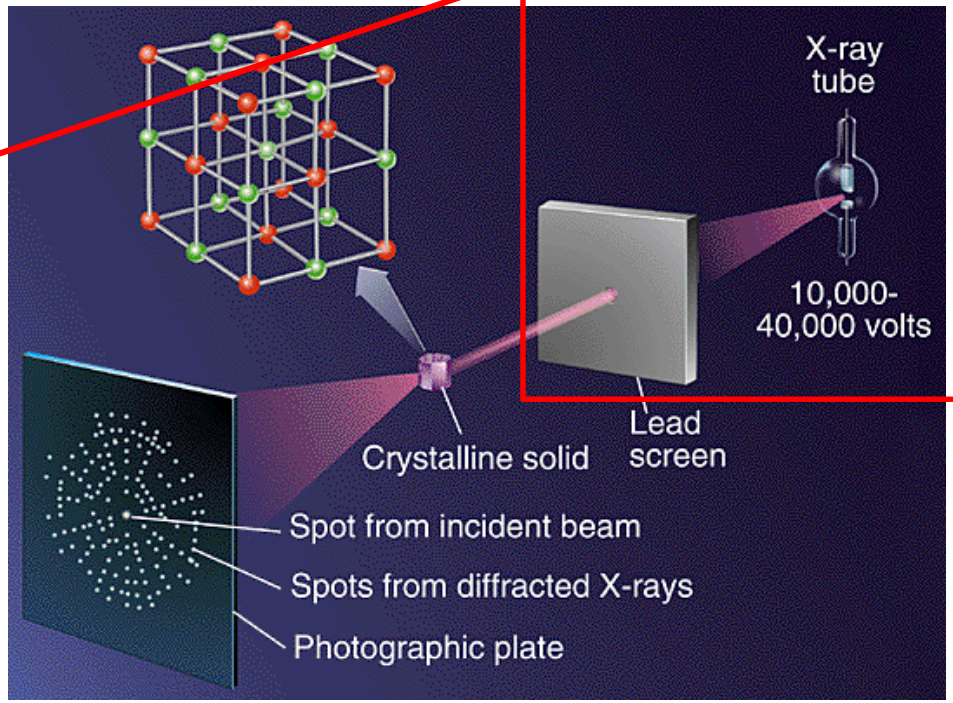


Figure: http://www.scienceiscool.org/solids/intro.html (dead link)

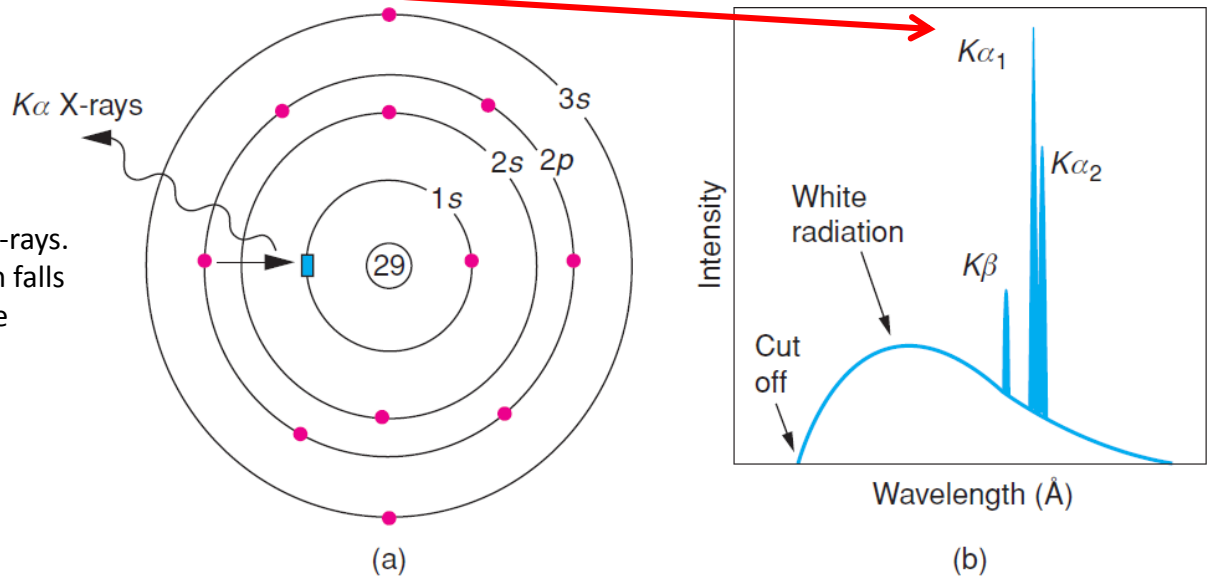


Figure 5.3. (a) Generation of Cu Kα X-rays. A 1s electron is ionised, a 2p electron falls into the empty 1s level (blue) and the excess energy is released as X-rays.

(b) X-ray emission spectrum of Cu

Ref: West p. 233

Bragg's law

- Consider crystals as built up in planes acting as a semi-transparent mirrors
- ***Bragg's law***: $2d \sin\theta = n\lambda$, where n = positive integer and λ = wavelength
- When **BL** satisfied, the reflected beams are in-phase and ***interfere constructively***, giving rise to a ***diffraction pattern***, that can be used to solve the crystal structure
- For some simple crystal structures, the planes also correspond to layers of atoms, but this is not generally the case (they are a concept, not physical reality)!

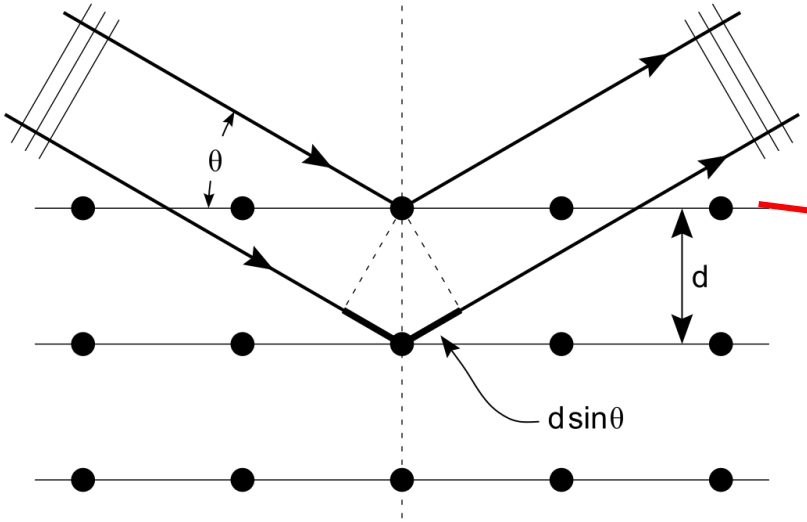


Figure: Wikipedia

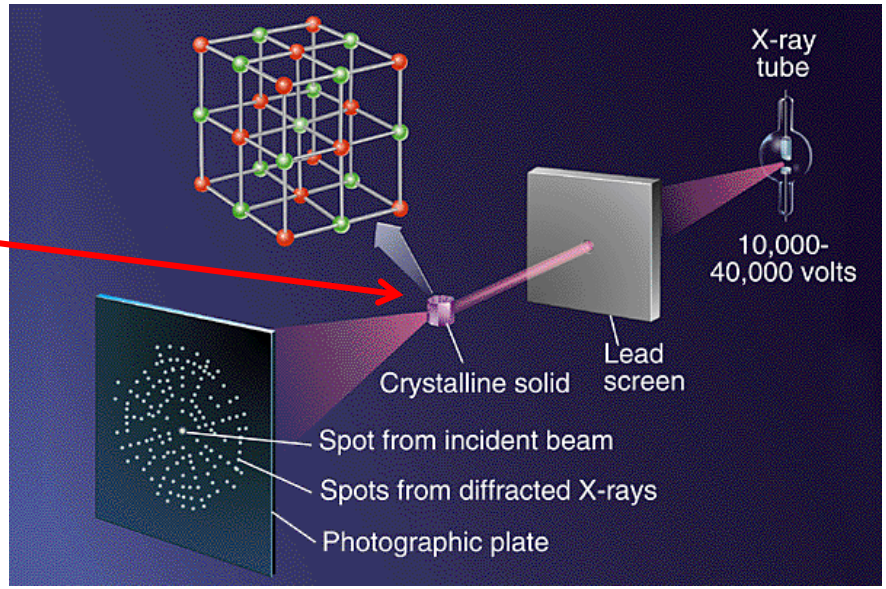
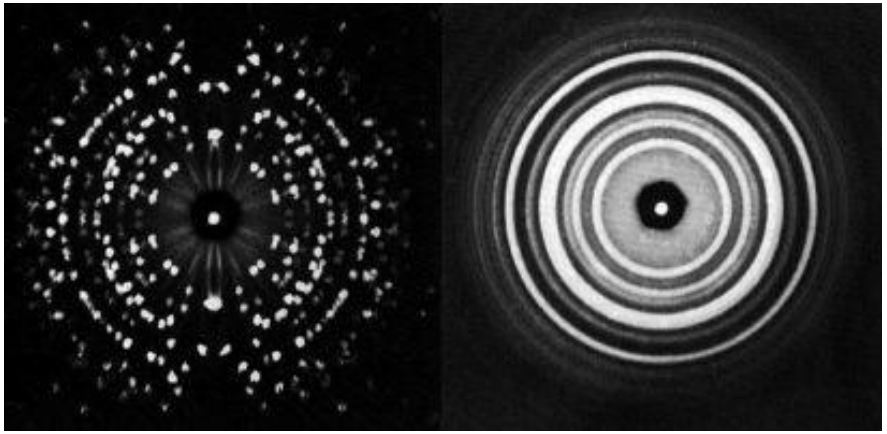


Figure: http://www.scienceiscool.org/solids/intro.html (dead link)

Single crystal vs. powder X-ray

- X-ray diffraction pattern of aluminum single crystal (left) and powder (right)
- Polycrystalline powder sample has random orientation of crystallites
- 1D summation of 3D diffraction process!
- The crystal structure might be deduced from a powder pattern with ***Rietveld*** refinement (typically requires a good model structure)
- X-ray diffraction powder pattern of crystalline (top) and amorphous (bottom) material

Figure: Susan Lehman / physics.wooster.edu



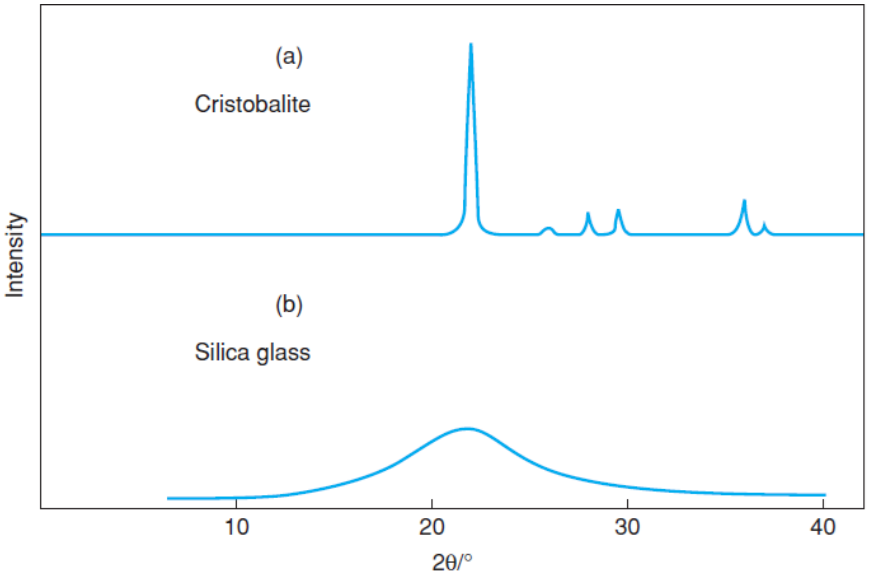
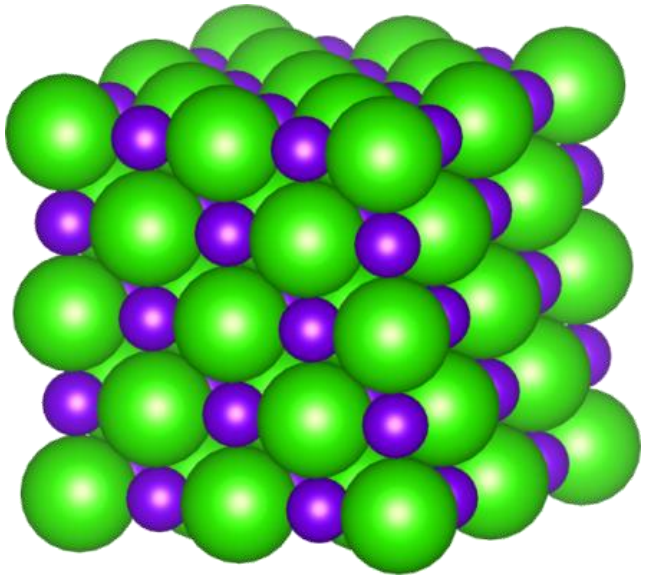


Figure 5.15 *X-ray powder diffraction patterns of (a) cristobalite and (b) glassy SiO_2; Cu Kα radiation.*

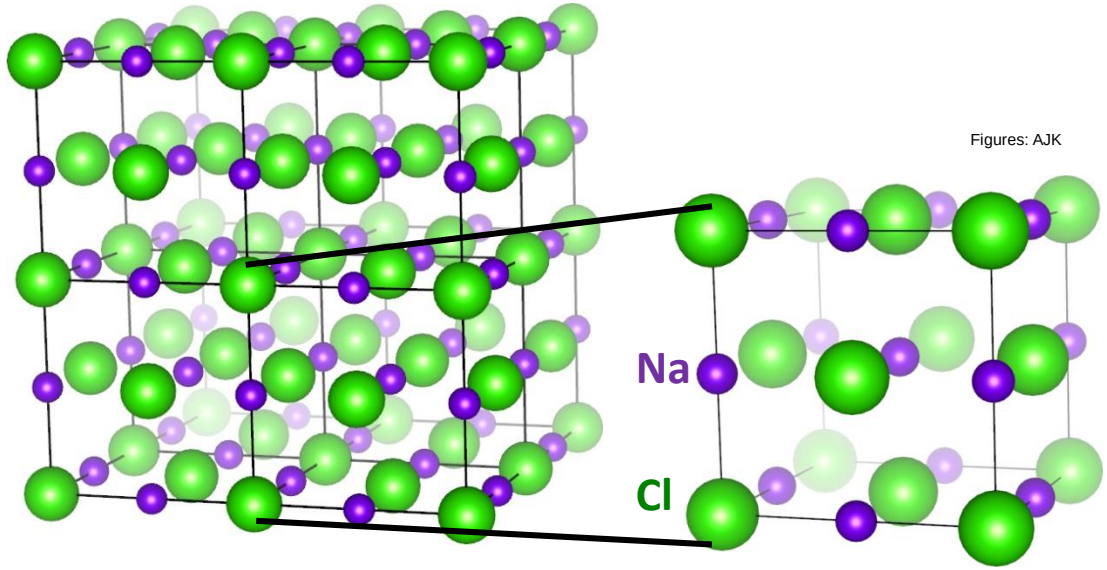
Ref: West p. 245

Unit cell

- ***Crystal***: Regular arrangement of atoms in three dimensions
- The regular arrangement can be represented by a repeat unit called the ***unit cell***
- ***Unit cell***: The smallest repeating unit which shows the ***full symmetry*** of the crystal



NaCl crystal: Regular arrangement of Na and Cl (space-filling representation)



NaCl crystal (non-space-filling representation

NaCl unit cell

Crystal systems

Figure 1.3 *(a) The seven crystal systems and their unit cell shapes;* **a, b, c, α, β, γ = Lattice parameters**

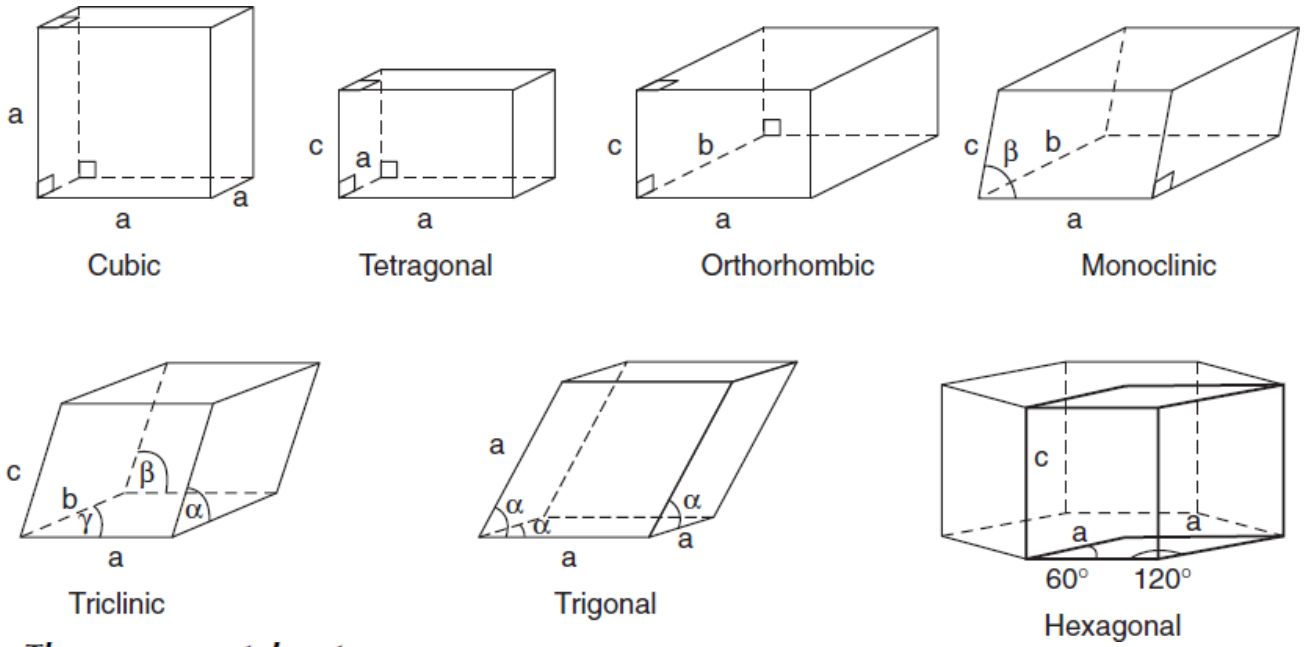


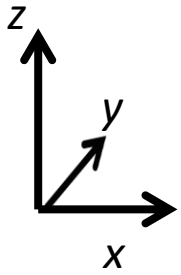
Table 1.1 ***The seven crystal systems***

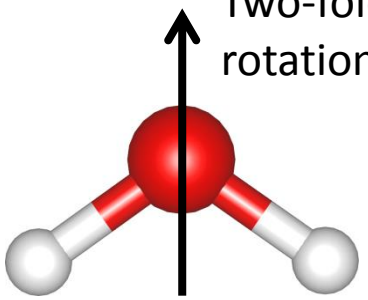
Crystal system	Unit cell shape[b]	Essential symmetry	Allowed lattices
Cubic	$a = b = c, \alpha = \beta = \gamma = 90°$	Four threefold axes	P, F, I
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90°$	One fourfold axis	P, I
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90°$	Three twofold axes or mirror planes	P, F, I, A (B or C)
Hexagonal	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	One sixfold axis	P
Trigonal (a)	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	One threefold axis	P
Trigonal (b)	$a = b = c, \alpha = \beta = \gamma \neq 90°$	One threefold axis	R
Monoclinic[a]	$a \neq b \neq c, \alpha = \gamma = 90°, \beta \neq 90°$	One twofold axis or mirror plane	P, C
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$	None	P

Ref: West p. 3-4

Symmetry

- The most characteristic feature of any crystal structure is its ***symmetry***
  1. ***Point group symmetry*** (also relevant for molecules)
  2. Translational symmetry of the crystal lattice (only in crystals)
- ***Symmetry elements***:
  - Mirror plane, inversion center, proper axis, improper axis, and identity
- ***Symmetry operation***: The actual process of applying the symmetry element.
- A symmetry operation transfers an object into a new spatial position that cannot be distinguished from its original position
- Extremely helpful resource for PG symmetry: http://symmetry.otterbein.edu/

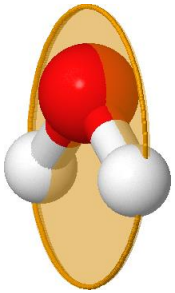




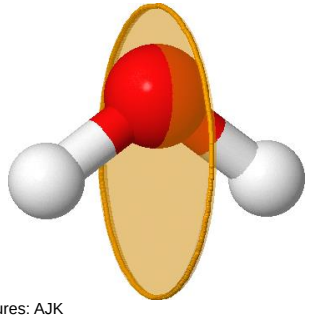
Two-fold proper rotation axis (C_2)

H_2O (point group C_{2v})

Reflection (mirror) plane (σ_{yz})

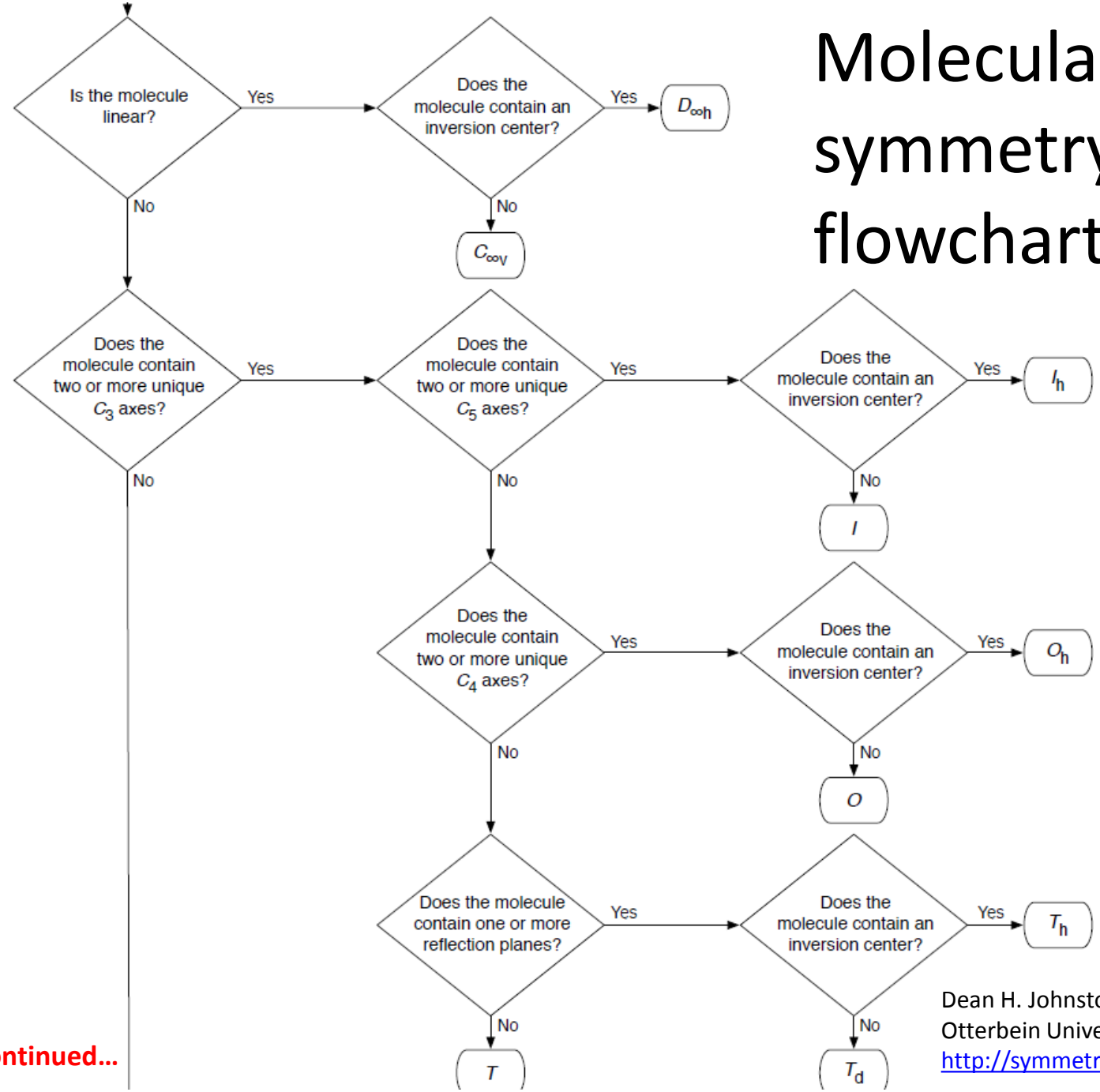


Reflection (mirror) plane (σ_{xz})

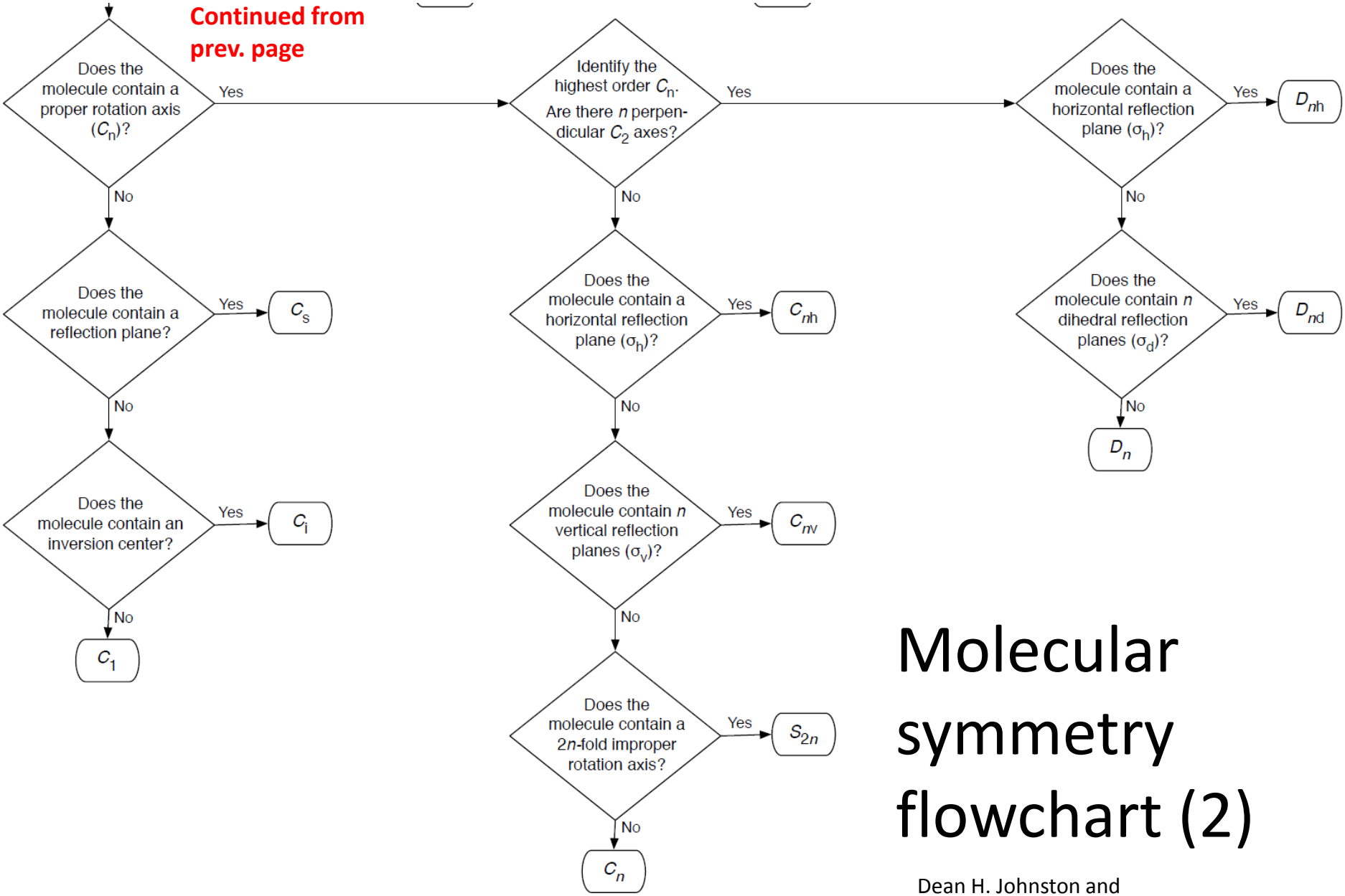


Figures: AJK

Molecular symmetry flowchart (1)



To be continued…



Molecular symmetry flowchart (2)

Dean H. Johnston and
Otterbein University
http://symmetry.otterbein.edu/

Symmetry elements in crystals

- The shape of the unit cell is not enough to determine the crystal system. It is the symmetry of the unit cell that really determines the crystal system
  - For example, a true cubic structure always shows four 3-fold symmetry axes
  - A "pseudocubic" crystal structure could have lattice parameters $a = b = c$ and $\alpha = \beta = \gamma = 90°$, but it would not possess the correct cubic symmetry
- Crystals may display rotational symmetries 2, 3, 4 and 6, not others!
- In crystallography, the symmetries are labeled with ***Hermann–Mauguin*** symbols

Table 1.2 ***Symmetry elements***

	Symmetry element	Hermann–Mauguin symbols (crystallography)	Schönflies symbols (spectroscopy)
Point symmetry At least one point stays unchanged during the symmetry operation	Mirror plane	m	σ_v, σ_h
	Rotation axis	$n = 2, 3, 4, 6$	C_n (C_2, C_3, etc.)
	Inversion axis	$\bar{n}$ ($= \bar{1}, \bar{2}$, etc.)	–
	Alternating axis[a]	–	S_n (S_1, S_2, etc.)
	Centre of symmetry	$\bar{1}$	i
Space symmetry Includes translation	Glide plane	a, b, c, d, n	–
	Screw axis	2_1, 3_1, etc.	–

[a] The *alternating axis* is a combination of rotation (n-fold) and reflection perpendicular to the rotation axis. It is little used in crystallography.

Ref: West p. 5

Inversion axis

- Denoted by $\bar{n}$. Rotation of 360° / *n* followed by inversion.
- $\bar{1}$ = equal to inversion center
- $\bar{2}$ = equal to mirror plane (*m*)
- $\bar{3}$, $\bar{4}$, $\bar{6}$ are actual inversion axes
- For example, $\bar{3}$ inversion axis (equal to S_6 improper rotation):

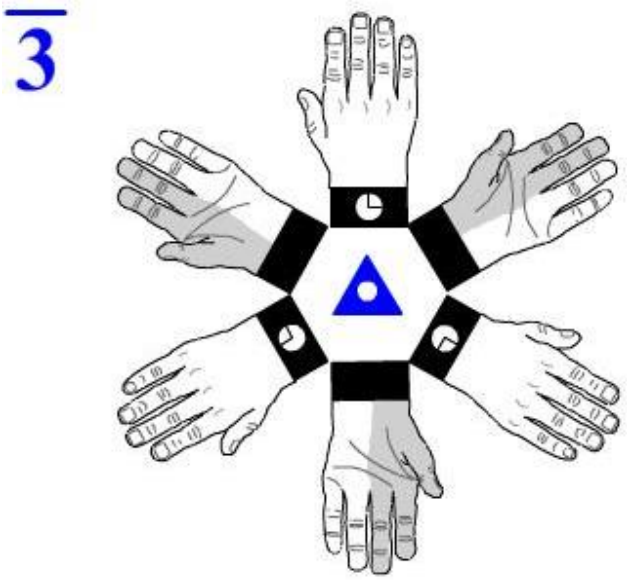


Figure: Margaret E. Kastner,
http://www.crystallographiccourseware.com/

Glide plane

- Reflection followed by a translation
  - Simple glide planes are denoted as *a*, *b*, *c* (axis of the glide)
  - *n* glide: reflection followed by translation of 1/2 along ***two*** cell edges
  - *d* glide (diamond glide): reflection followed by translation of 1/4 along ***two*** cell edges

Glide plane (parallel to *a*, reflection followed by a translation of ½*a*)

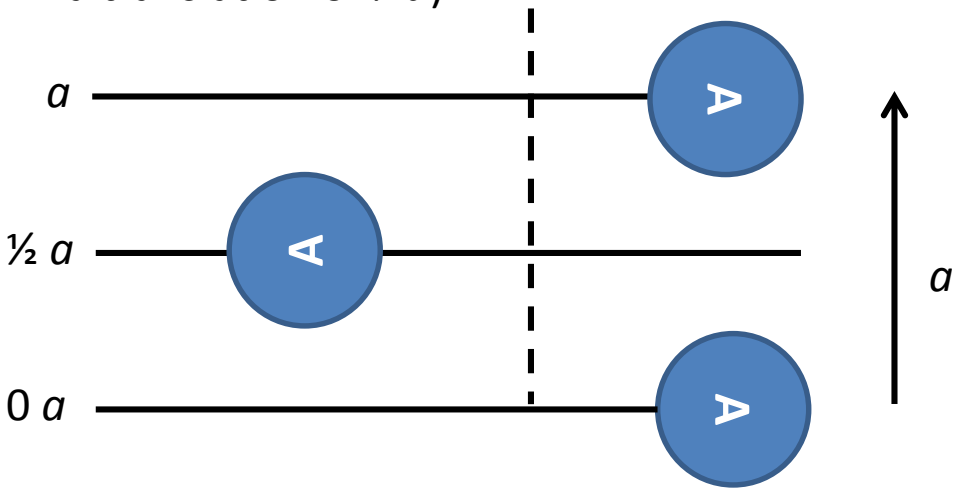
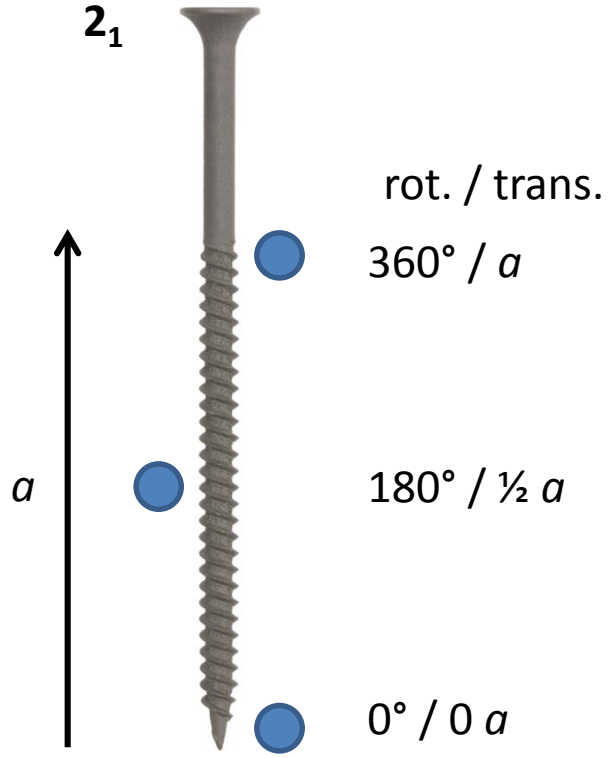


Figure: AJK

Screw axis

- Combination of rotation and translation, denoted as x_y:
  - Rotation of 360° / *x*; translation of *y* / *x* units along the screw axis
  - 2_1 screw axis: rotation of 360° / 2 = 180°; translation of 1/2 units
  - 4_2 screw axis: rotation of 360° / 4 = 90°; translation of 2/4 = 1/2 units



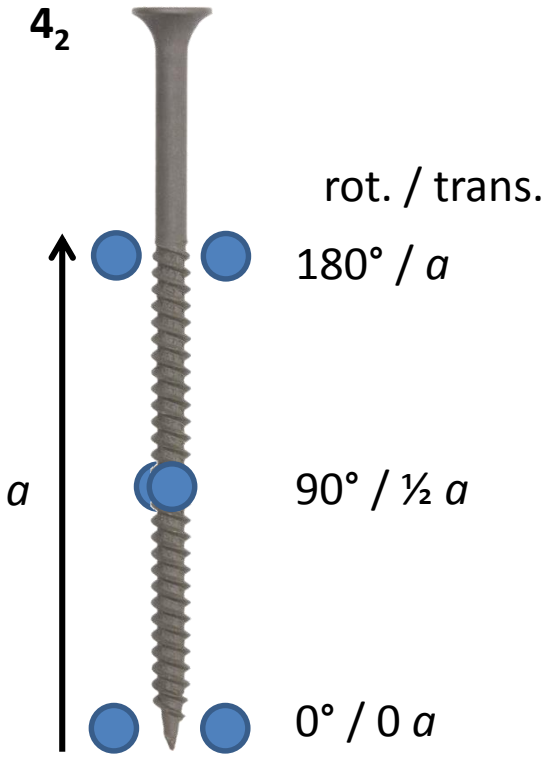


Figure: AJK. Inpisred by: Margaret E. Kastner, http://www.crystallographiccourseware.com/

Screw: pngimg.com

Crystal classes

- The seven crystal systems consist of 32 crystal classes corresponding to the 32 crystallographic point groups

Crystal system	Crystal classes (point groups) in Hermann-Mauguin notation	Crystal classes (point groups) in Schönflies notation
Triclinic	1, $\bar{1}$	C_1, C_i
Monoclinic	2, *m*, 2/*m*	C_2, C_s, C_{2h}
Orthorhombic	222, *mm*2, *mmm*	D_2, C_{2v}, D_{2h}
Tetragonal	4, $\bar{4}$, 4/*m*, 422, 4*mm*, $\bar{4}$2*m*, 4/*mmm*	C_4, S_4, C_{4h}, D_4, C_{4v}, D_{2d}, D_{4h}
Trigonal	3, $\bar{3}$, 32, 3*m*, $\bar{3}m$	C_3, S_6 (C_{3i}), D_3, C_{3v}, D_{3d}
Hexagonal	6, $\bar{6}$, 6/*m*, 622, 6*mm*, $\bar{6}$*m*2, 6/*mmm*	C_6, C_{3h}, C_{6h}, D_6, C_{6v}, D_{3h}, D_{6h}
Cubic	23, $\bar{4}$3*m*, *m*$\bar{3}$, 432, *m*$\bar{3}$*m*	*T*, T_d, T_h, *O*, O_h

Ref: Müller p. 24, Wikipedia

Lattice

- The most characteristic feature of any crystal structure is its ***symmetry***
  1. Point group symmetry (discussed above)
  2. ***Translational symmetry*** of the ***crystal lattice***
- Crystal structure = ***basis*** (atoms) + crystal lattice

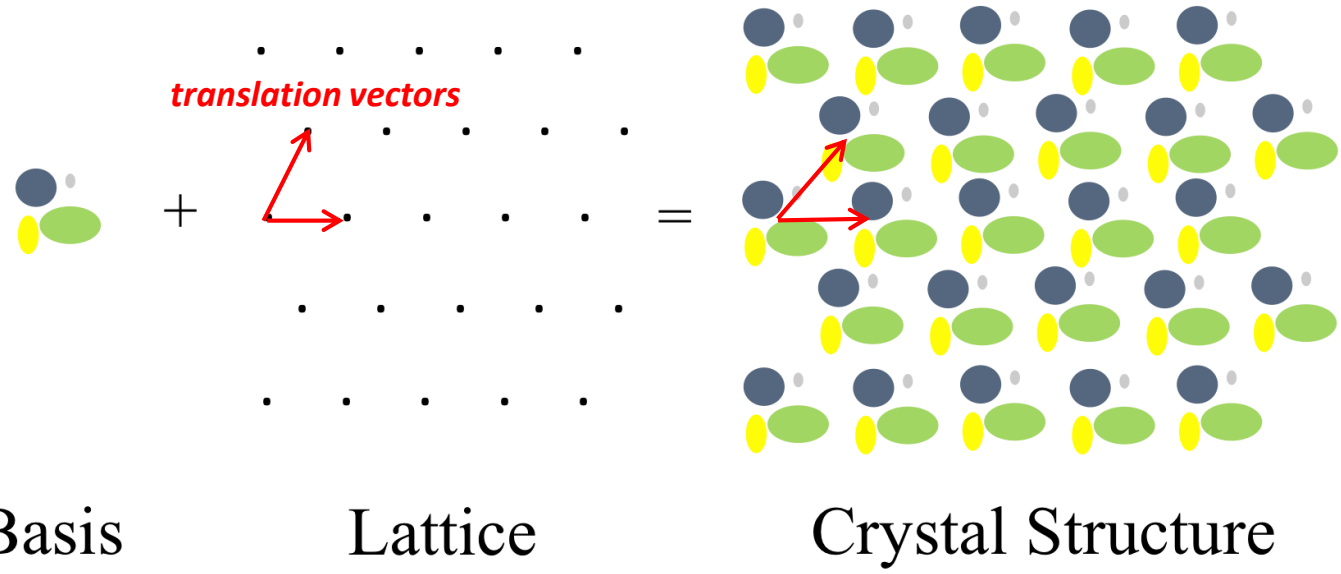
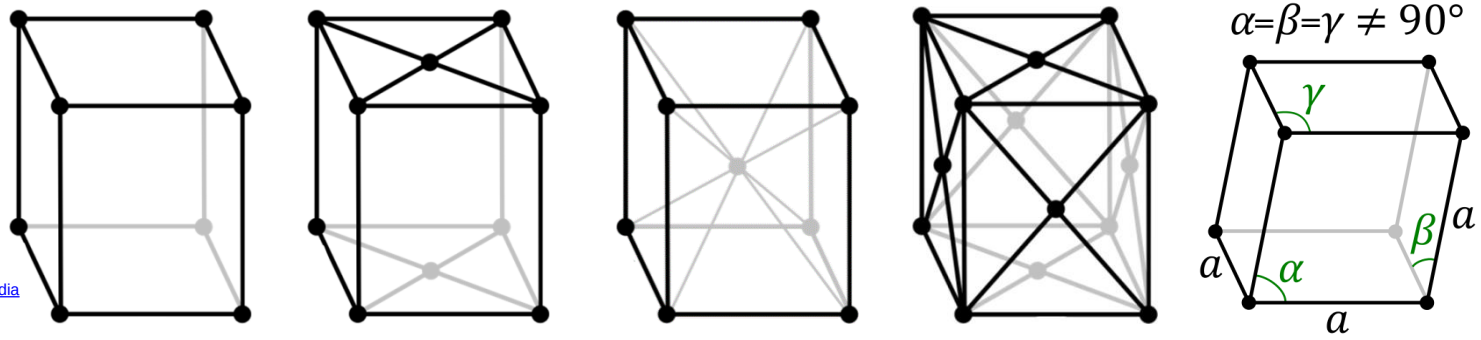


Figure: Andreas Mulyo

Lattice types

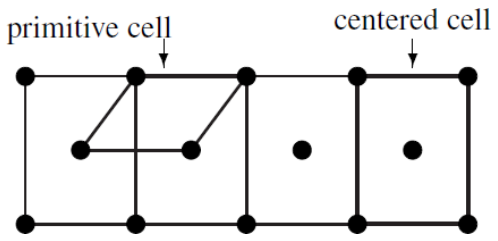
- Every crystal structure belongs to one of five ***lattice types***:
  - The balls are lattice points, ***not*** atoms!



Figures: Wikipedia

Lattice type	Primitive	Base-centered	Body-centered	Face-centered	Rhombohedral
Symbol	*P*	*A* / *B* / *C*	*I*	*F*	*R*
V(C-cell)/*V*(P-cell)	1	2	2	4	3

- ***Primitive unit cell***: unit cell with the smallest possible volume
- ***Centered unit cell***: the smallest repeating unit which shows the full symmetry of the crystal
- Except for the lattice type *P*, the centered unit cell is 2, 3, or 4 times larger than the primitive cell (table: *V(C-cell)/V(P-cell)*)
- 7 crystal systems and 5 lattice types -> 14 ***Bravais lattices***

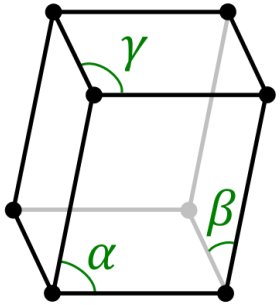


Ref: Müller p. 8

Bravais lattices (1)

Triclinic

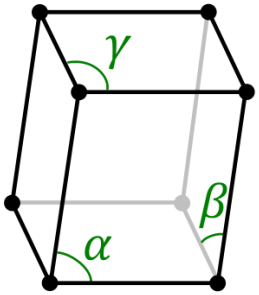
$\alpha, \beta, \gamma \neq 90°$



P

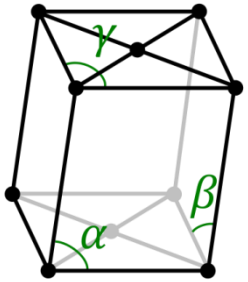
Monoclinic

$\beta \neq 90°$
$\alpha, \gamma = 90°$



P

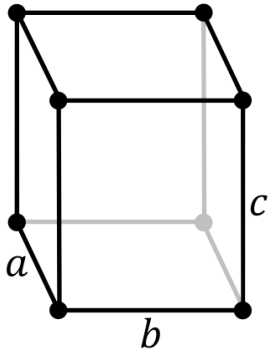
$\beta \neq 90°$
$\alpha, \gamma = 90°$



C

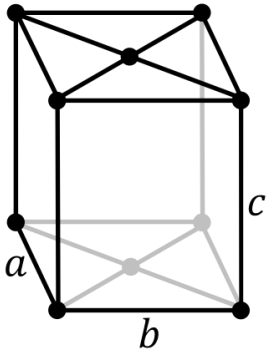
Orthorhombic

$a \neq b \neq c$



P

$a \neq b \neq c$



C

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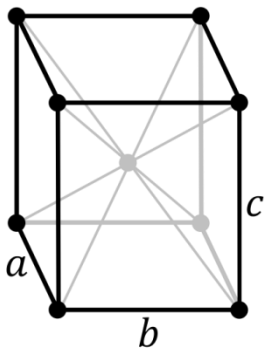
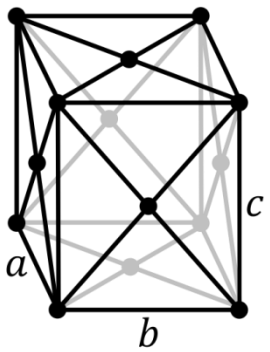


I

$a \neq b \neq c$

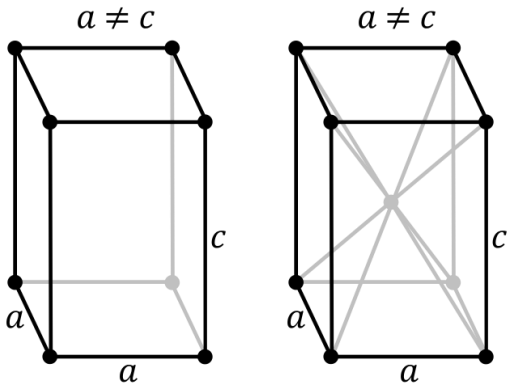


F

Figures: Wikipedia

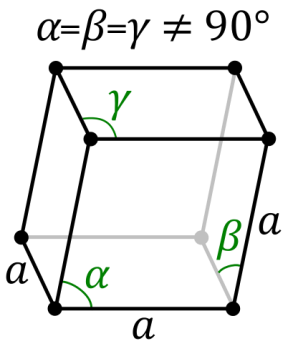
Bravais lattices (2)

Tetragonal



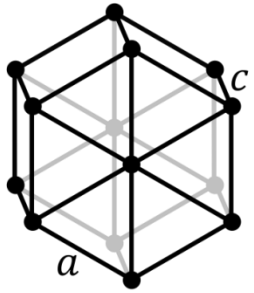
P ***I***

Rhombohedral



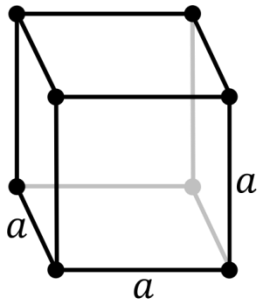
R

Hexagonal

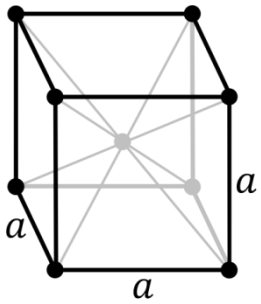


P

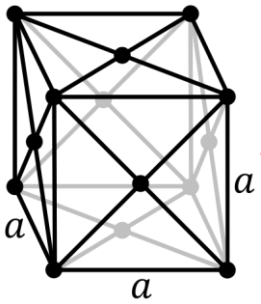
Cubic



P

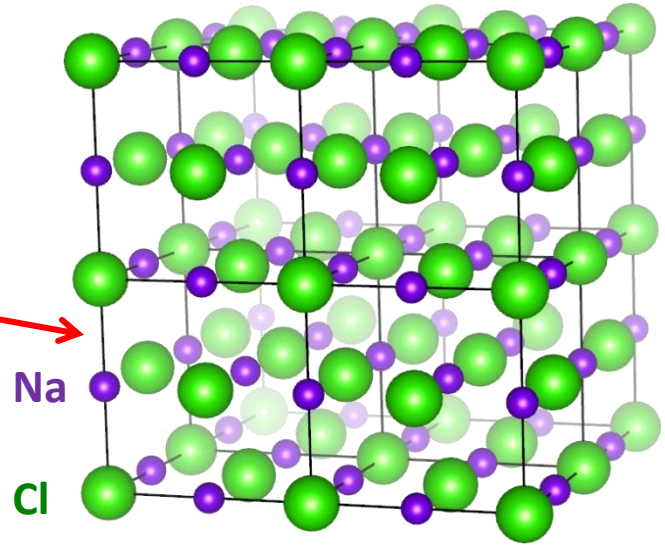


I (bcc)



F (fcc)

Figure: AJK



fcc, basis: Cl + Na

Figures: Wikipedia

Space groups

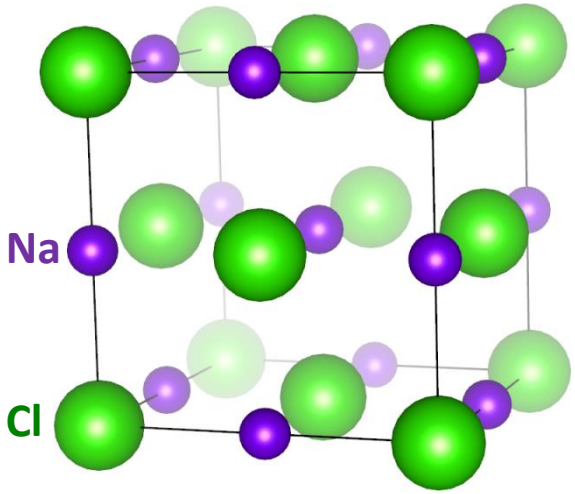
- The **32** crystal classes and **14** Bravais lattices give rise to **230** space groups
- The Hermann-Mauguin symbol for the space group of NaCl: ***Fm$\bar{3}$m*** (or ***Fm-3m***)
- The symbol begins with a capital letter *P, A, B, C, F, I* or *R,* specifying the presence of ***translational symmetry*** in three dimensions and the lattice type (***centering***)
- The letter is followed by a listing of the other symmetry elements
- Some examples:
  - All ***triclinic*** space groups: *P*1 and *P*-1
  - Some ***monoclinic*** space groups: *P*2, *Pm*, *C*2/*c*
  - Some ***hexagonal*** space groups: *P*6, *P*6/*mmm*, *P*6/*mcc*
  - Some ***cubic*** space groups: *Pm*-3*m*, *Im*-3*m*
- Note that some space groups can be defined with ***alternate axes*** and/or ***origin*** (see e.g. orthorhombic SGs in http://img.chem.ucl.ac.uk/sgp/large/ortho.htm)
- Everything about space groups: International Tables of Crystallography
- Good resource: http://img.chem.ucl.ac.uk/sgp/large/sgp.htm
- Wikipedia: https://en.wikipedia.org/wiki/List_of_space_groups

Defining a crystal structure

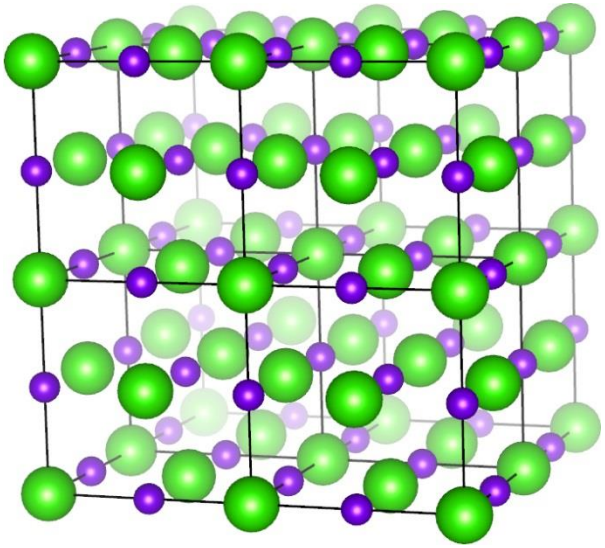
- A crystal structure is defined by
  - Space group
  - Lattice parameters
  - Atomic coordinates (positions) in fractional coordinates ($0.0 \leq x,y,z < 1.0$)
  - Normally only ***symmetry-independent*** atoms in the ***asymmetric unit*** are listed
- For example, NaCl (ICSD code 655785)
  - ***Fm*-3*m***
  - $a = b = c =$ **5.6402** (Å); $\alpha = \beta = \gamma =$ **90°**
  - Atomic coordinates (x, y, z): **Cl**: 0.0, 0.0, 0.0; **Na**: 0.5, 0.5, 0.5
- Typically, crystal structures are distributed in Crystallographic Information Files (CIF)
- A ***definition*** of a crystal structure is not usually enough to understand the real chemistry. For this, we need a ***description*** of the crystal structure
  - Concepts such as bonding, packing of spheres, coordination, polyhedra, ...

Formula units (Z)

- Counting the contents of a unit cell for NaCl:
- 8 Cl^- ions in the 8 vertices, each belonging to 8 adjacent cells = 8/8 = **1** Cl^- ion in total
- 6 Cl^- ions in the 6 centers of the faces, each belonging to two cells = 6/2 = **3** Cl^- ions
- **1** Na^+ ion in the center of the cell, not shared with other cells
- 12 Na^+ ions in the centers of the 12 edges, each belonging to 4 cells = 12 / 4 = 3 Na^+ ions
- In total **4** Na^+ ions and **4** Cl^- ions
  - NaCl is said to have **4** ”formula units” per unit cell
  - Denoted with $Z = 4$



Figures: AJK



Summary of crystal structures

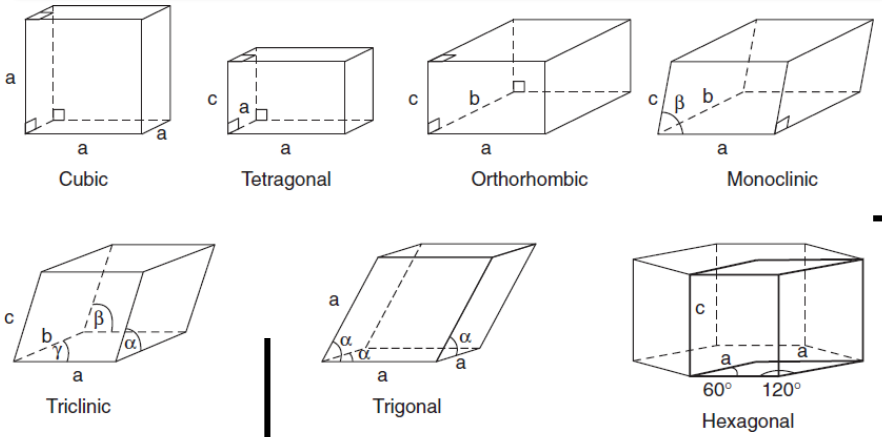
- Crystal systems (7 of them)
- Crystal classes / crystallographic point groups (32 of them)
- Lattice types (5 of them)
- Crystal systems + lattice types -> Bravais lattices (14 of them)
- Crystal classes + Bravais lattices -> Space groups (230 of them)

Table 1.1 ***The seven crystal systems***

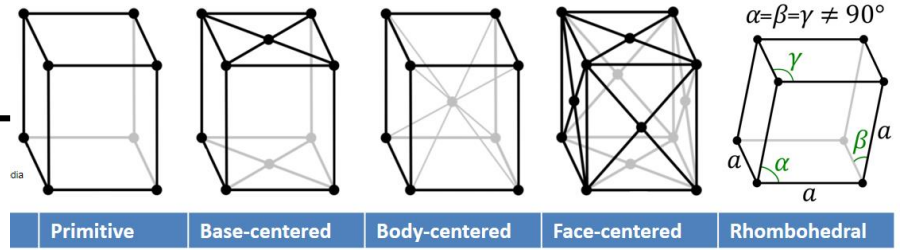
Crystal system	Unit cell shape[b]	Essential symmetry	Allowed lattices
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	Four threefold axes	P, F, I
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	One fourfold axis	P, I
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	Three twofold axes or mirror planes	P, F, I, A (B or C)
Hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	One sixfold axis	P
Trigonal (a)	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	One threefold axis	P
Trigonal (b)	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	One threefold axis	R
Monoclinic[a]	$a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	One twofold axis or mirror plane	P, C
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	None	P

Ref: West p. 3-4

Crystal systems (7 of them)



Lattice types (5 of them)

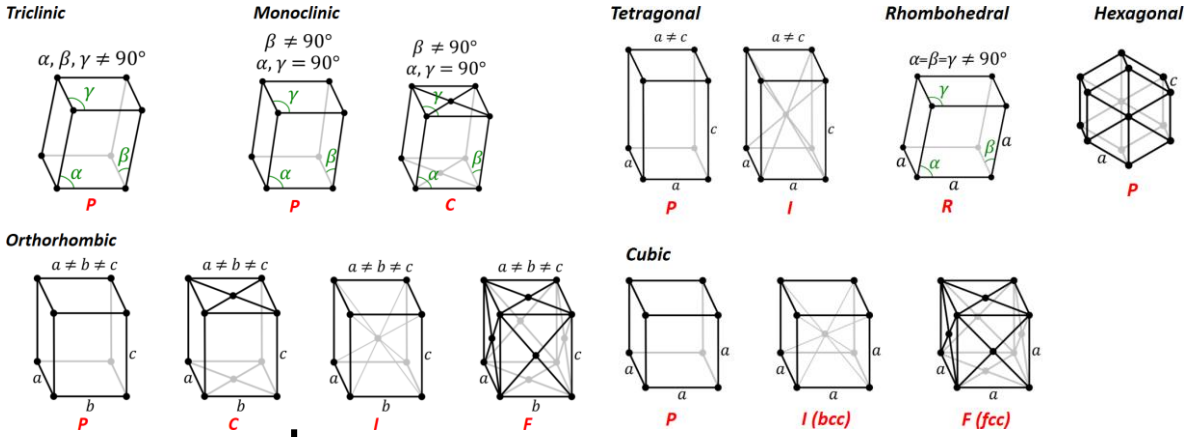


	Primitive	Base-centered	Body-centered	Face-centered	Rhombohedral

Crystal classes (32 of them)

Crystal system	Crystal classes (point groups) in Hermann-Mauguin notation
Triclinic	1, $\bar{1}$
Monoclinic	2, *m*, 2/*m*
Orthorhombic	222, *mm*2, *mmm*
Tetragonal	4, $\bar{4}$, 4/*m*, 422, 4*mm*, $\bar{4}$2*m*, 4/*mmm*
Trigonal	3, $\bar{3}$, 32, 3*m*, $\bar{3}m$
Hexagonal	6, $\bar{6}$, 6/*m*, 622, 6*mm*, $\bar{6}$*m*2, 6/*mmm*
Cubic	23, $\bar{4}3m$, $m\bar{3}$, 432, $m\bar{3}m$

Bravais lattices (14 of them)



Space Groups (230 of them)

Summary: AJK. Individual figures from Wikipedia and West (p 3.)

Extra 1: Trigonal crystal system

Hexagonal crystal family

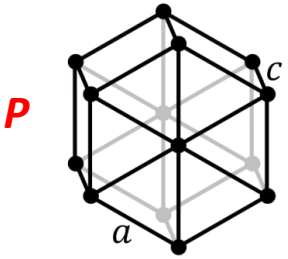
Hexagonal crystal system (27 space groups)

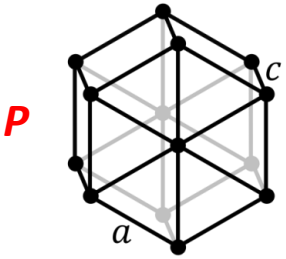
Trigonal crystal system (25 space groups)

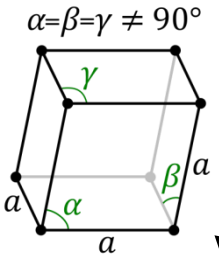
Hexagonal Bravais lattice (27 space groups)

Hexagonal Bravais lattice (18 space groups)

Rhombohedral Bravais lattice (7 space groups)





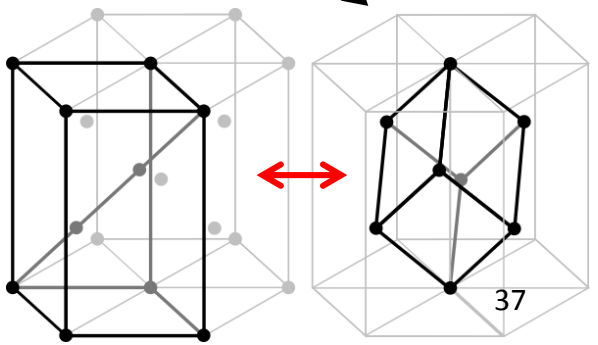


Can also be described with hexagonal unit cell (3 x larger)

Figures: Wikipedia

Table 1.1 ***The seven crystal systems***

Crystal system	Unit cell shape[b]	Essential symmetry	Allowed lattices
Cubic	$a = b = c, \alpha = \beta = \gamma = 90°$	Four threefold axes	P, F, I
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90°$	One fourfold axis	P, I
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90°$	Three twofold axes or mirror planes	P, F, I, A (B or C)
Hexagonal	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	One sixfold axis	P
Trigonal (a)	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	One threefold axis	P
Trigonal (b)	$a = b = c, \alpha = \beta = \gamma \neq 90°$	One threefold axis	R
Monoclinic[a]	$a \neq b \neq c, \alpha = \gamma = 90°, \beta \neq 90°$	One twofold axis or mirror plane	P, C
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$	None	P



Extra 2: Perfect crystals do not exist

- Crystal structures from X-ray diffraction are ”average” structures
- Real crystals possess defects (**lecture 13**)
- Point defects, line defects, grain boundaries, stacking faults, bulk defects, etc.
- Some defects can be characterized using techniques other than XRD (**lecture 8**)

Figure 2.2 ***2D representation of a Schottky defect with cation and anion vacancies.***

Ref: West p. 83

Extra 3: Quasicrystals (1)

- Quasicrystals exhibit long-range order, but do not have translational periodicity
- Quasicrystals can show ”forbidden” rotational symmetries of 5, 8, 10, 12, etc.
- Discovered by Daniel Schechtman in 1982, Nobel prize 2011 (link)

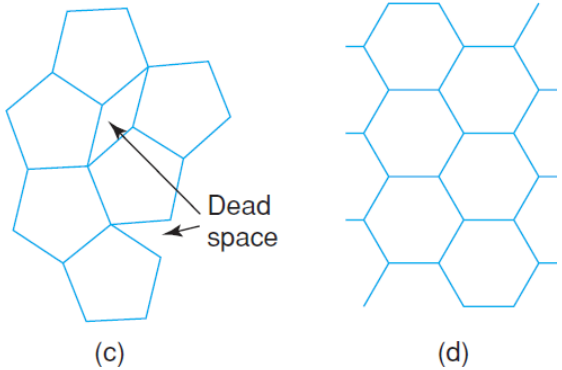


Figure 1.4. (c) the impossibility of forming a complete layer of pentagons; (d) a complete layer of hexagons

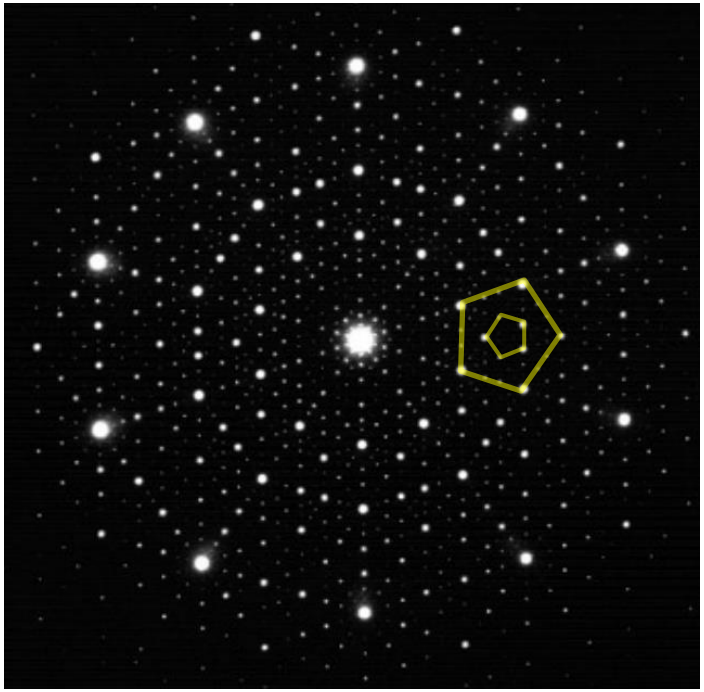


Figure: Nobel committee

Electron diffraction pattern from an icosahedral quasicrystal

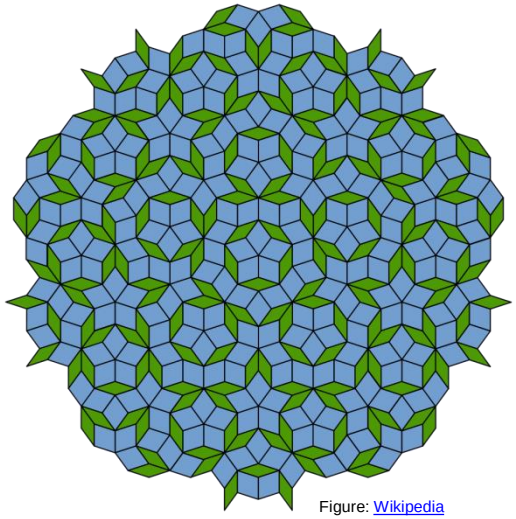


Figure: Wikipedia

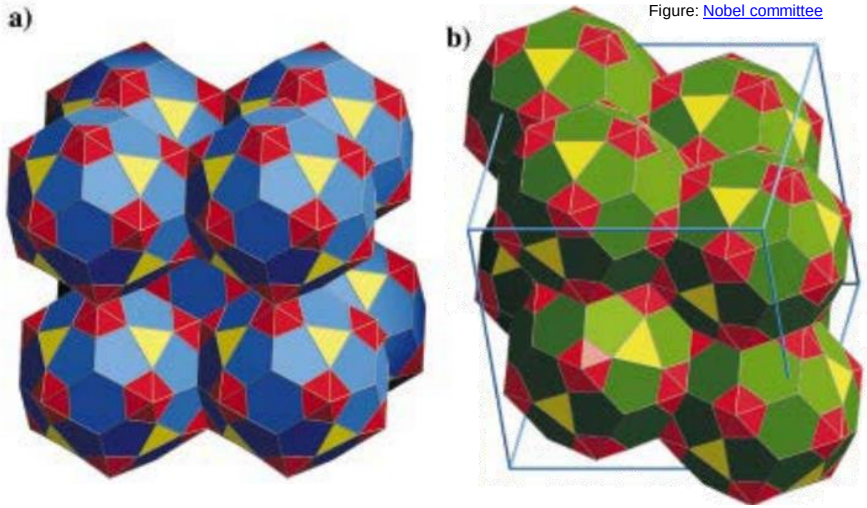
Penrose tiling (no translational periodicity)

Ref: West p. 5-6

Extra 3: Quasicrystals (2)

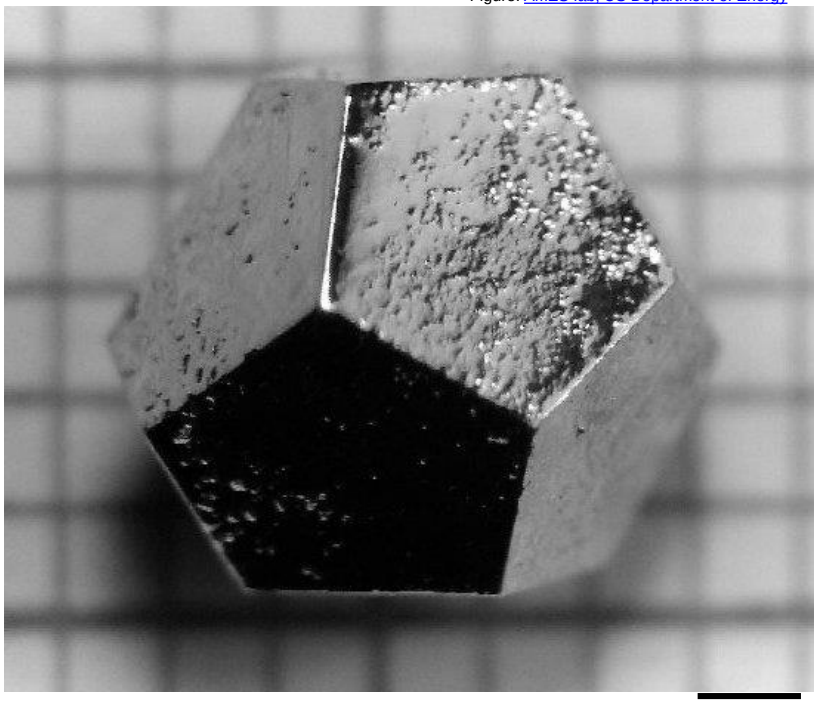
- Icosahedral symmetry is allowed together with translational symmetry in 6-dimensional space
- Refinement of quasicrystal models involves the refinement of the position and shape of the atomic surfaces in 6-dimensional space for icosahedral quasicrystals

Figure: Nobel committee



Polyhedral arrangements in icosahedral quasicrystal ***approximants*** in the system Ca-Cd (*Angew. Chem.* **2001**, *40*, 4037-4039)

Figure: AMES lab, US Department of Energy



Ho-Mg-Zn dodecahedral quasicrystal (*Phys. Rev. B* **1999**, *59*, 308–321)